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Characterisation of Thin Films $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ Prepared by Selenisation of Magnetron Sputtered Metallic Precursors

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ABSTRACT

Thin films of $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ have been produced by the selenisation of magnetron sputtered Cu/In/Al precursor layers using elemental selenium and the chemical and physical properties of the layers have been determined for different conditions of synthesis. For optimum conditions of synthesis it was found possible to produce single phase films with the chalcopyrite structure. These films were pinhole free, had good adhesion and were conformal to the substrate. The films had uniform depth profiles as determined using the MiniSIMS. The layers were highly photoactive, indicating that they have the potential to be used to fabricate thin film photovoltaic solar cell devices.

INTRODUCTION

Chalcopyrite CuInSe_2 (CIS) based solar cells associated with Ga and S have achieved the highest level of performance to date for single junction polycrystalline thin film technology. Current state of the art $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) solar devices exhibit efficiencies up to 19.5% [1]. However this material has a relatively low bandgap ($E_g = 1.2$ eV for $x = 0.3$) compared to the 1.5 eV required for optimum solar energy conversion. CIGS-based devices fabricated with $E_g > 1.3$ eV ($x > 0.5$) are found to have substantially reduced efficiencies [2]. This is attributed to fill factor and open circuit voltage losses arising from increased defect density and stronger interfacial recombination when the Ga content is increased. The need for higher bandgap material ($E_g > 1.5$ eV) is driven by the desire to produce (i) higher efficiency devices and (ii) wider energy bandgap cells, for use as the upper cells in multi-junction devices. Substituting Ga by Al makes it possible to produce $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ (CIAS) material with the same energy bandgap as CIGS but using less Al. This is because the variation of E_g with Al content is up to 2.7 eV for CuAlSe_2 compared to 1.7 eV for CuGaSe_2 . Indeed CIAS solar cells with $E_g = 1.16$ eV and $x = 0.13$ have been produced with efficiencies of 16.9% [3]. This compares to 16.5% for CIGS deposited under similar conditions but with $x = 0.26$ ($E_g = 1.16$ eV) [3]. In this work we have investigated the production of CIAS thin films by a 2 stage process that involves the deposition of Cu/In/Al metallic precursor layers followed by annealing in a selenium environment to synthesise the compound. In principle this method promises improved scalability for commercial production compared to other deposition methods. It could also lead to the production of wider energy bandgap CIAS thin films.

EXPERIMENTAL DETAILS

The Cu/In/Al metallic precursor layers were deposited onto soda lime glass or Mo-coated soda lime glass slides using magnetron sputtering. The base pressure in the sputtering chamber was better than 5×10^{-7} mbar and high purity 5N Cu, In and Al targets were used. The precursor layers were produced by the sequential depositions of Cu, In and Al together with rotation of the substrates to ensure good uniformity and intermixing of the elements. The Cu/In/Al precursors, 700-800 nm thick were deposited on top of a 10 nm Cu seed layer. Compositions in the range $0.6 < \text{Cu}/(\text{In}+\text{Al}) < 1.4$ and $0.1 < \text{Al}/(\text{In}+\text{Al}) < 0.7$ were produced and the variations in composition did not exceed 10% over a 76x76 mm area. Selected samples were coated with a Cu or In capping layer to protect the underlying precursor layers from oxidation when removed from the deposition system. Prior to the selenisation a selenium layer was deposited over the entire precursor surface. The selenisation was then carried out in a tube furnace in an Ar/Se atmosphere using an annealing temperature in the range of 500-550°C for an annealing time of 30 min.

The phases present and structure of each phase were investigated using X-ray diffraction (XRD) in a Siemens D-5000 diffractometer using the $\text{CuK}\alpha$ line. The surface morphology and topology of the films were observed using a FEI Quanta 200 scanning electron microscope (SEM) and semi-quantitative compositional analysis of the precursors performed using the energy dispersive X-ray analyzer connected to the SEM. Depth profiling and investigations of lateral uniformity of the layers were investigated in detail using a bench-top Millbrook MiniSIMS system. The photo-activity of the CIAS films was photoelectrochemically measured by illuminating the sample in contact with an aqueous europium nitrate solution. This technique enables the photo-activity of the films to be assessed without processing into a complete device [4]. Prior to immersion in the solution the samples were etched in 10% potassium cyanide solution. The measurements were then carried out in a three electrode configuration using a glass cell with an Ag/AgCl reference electrode and a platinum foil as a counter electrode.

RESULTS AND DISCUSSION

Precursor films

Figure 1 shows the XRD patterns of precursor films with $\text{Al}/(\text{In}+\text{Al}) = 0.18$ and 0.41 deposited on glass. For $x = 0.18$, the phases present were found to be Cu_yIn_z ($\text{Cu}_{11}\text{In}_9$, CuIn_2 and $\text{Cu}_{16}\text{In}_{11}$) and Al_aCu_b (AlCu , AlCu_3 , AlCu_4 and Al_4Cu_9) binaries and also elemental In. No InAl binary and CuInAl ternary phases are detected due to the negligible solubility of indium in aluminum and this is irrespective of the $\text{Cu}/(\text{In}+\text{Al})$ ratio. For higher Al content ($x = 0.41$) the XRD pattern mainly displayed the presence of Cu_yIn_z phases. The presence of Al is detected in the peak at $\sim 42^\circ$ which shifts to higher 2θ value due to the increase in Al content. When the Al content is further increased to $x = 0.65$ all the peaks in the range 15° - 75° are attributed to the Cu_yIn_z binary phases. This indicates that Al probably exists in the films in the form of precipitates or segregates at grain boundaries.

The film uniformity with depth is shown in figure 2 where a MiniSIMS depth profile is given for a sample with $x = 0.18$. The MiniSIMS system determines the relative distribution of the elements within a given sample and was not calibrated to give absolute concentrations. This

sample had been completed by a 100 nm In cap layer and this is seen in figure 2 indicated by the Cu signal close to zero and a lower Al count. The main part of the scan relates to the Cu/In/Al multilayer precursor and is indicated by a rise in the signal of the three elements. The change in the In profile is due to a change in the SIMS relative sensitivity factor (RSF) from the In matrix to the Cu/In/Al matrix. The depth profiles show a uniform distribution of the three elements. The interface between the precursor and the Mo back contact is delineated by the rise in the Mo signal and subsequently the fall of the other three traces. The apparent blurring of the CuInAl/Mo interface is attributed to a combination of (i) the rough surface morphology of the layer and (ii) the light implantation of the metal elements during the deposition. This shows that this technique can be employed for preparing and controlling the composition of the precursor and subsequently selenised films.

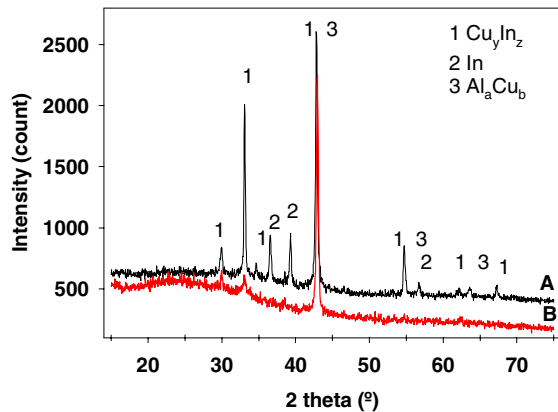


Figure 1. XRD pattern of precursor films deposited on glass with (A) Al/(In+Al) = 0.18 and Cu/(In+Al) = 0.8 and (B) Al/(In+Al) = 0.41 and Cu/(In+Al) = 1.2.

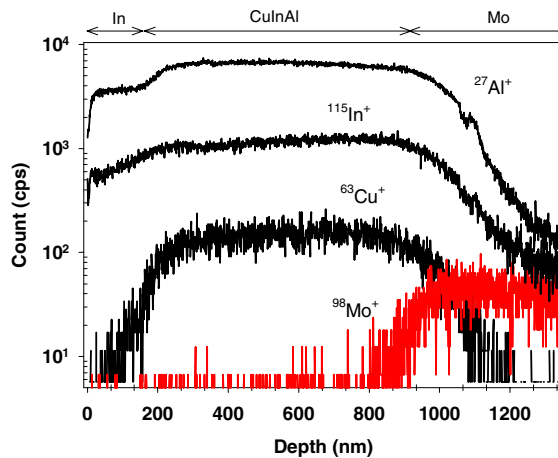


Figure 2. MiniSIMS depth profiles of a precursor film ($x = 0.18$).

Selenised films

Films coated with Se were selenised at 550°C for 30 min in an Ar-Se atmosphere. The films showed good adherence to the Mo substrate due to the very thin Cu seed layer. Figure 3a shows an XRD pattern of a selenised CIAS thin film. The film was found to be single phase and chalcopyrite in structure. The splitting of the (116/312) reflections indicates the good

crystallinity of the films. Figure 3b shows a detailed part of the XRD pattern near the (112) reflection for samples with different Al content. As the Al content incorporated into the CIS phase increases the peak shifts towards higher 2 theta values in accordance with the variations of lattice parameters with changing composition.

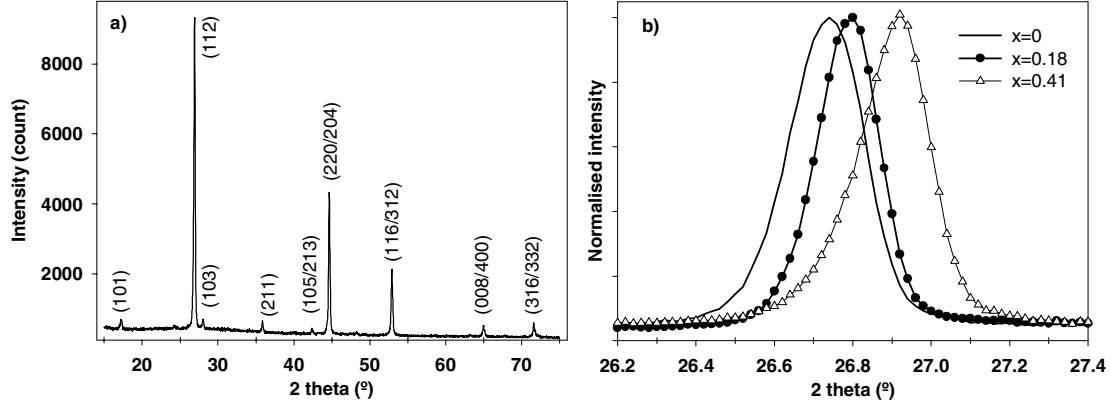


Figure 3. a) XRD spectrum of a $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ thin film ($x = 0.18$). b) Details of the (112) reflection as the Al content is increased.

A cross-sectional view and a plan view scanning electron micrograph of a CIAS thin film are given in figure 4. The cross-section image (figure 4a) shows that the layer is formed by large grains that are approximately equal in size to the thickness of the film and which extend unbroken from the top to the bottom of the CIAS film. This is a positive attribute for this semiconducting material as the large grains minimize the grain boundaries and their detrimental effect on conductivity and carrier recombination. Furthermore minority carriers can pass through the film without crossing a grain boundary. Figure 4b shows the surface morphology of the film and the compact structure made of large grains is confirmed. It was also observed that the surface lateral grain size is influenced by the Cu content similarly to CIS material. The higher Cu content in the film tends to yield large grain size, however for $\text{Cu}/(\text{In}+\text{Al}) > 1.3$ grains greater than $10\text{ }\mu\text{m}$ in size are formed and create a very rough surface.

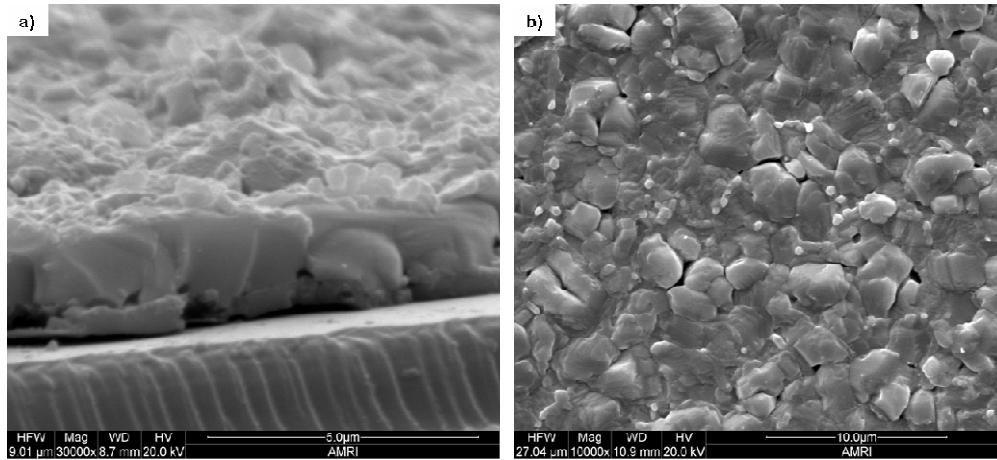


Figure 4. SEM micrographs of a $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$ ($x = 0.18$) thin film deposited on glass. a) Cross-section and b) top surface.

For some selenisations the resulting films behaved differently to that reported above in that the XRD pattern of the (112) peak did not shift as expected for CIAS formation and the absorption edge was measured to be 1 eV, *i.e.* consistent with that of pure CIS. The structural morphology of these films was, however, similar to that of the CIAS films. The possible reasons were that the films formed were (i) a mixture of CuInSe_2 and CuAlSe_2 compounds and (ii) there was incomplete conversion of the precursors [5, 6]. For the current study, although both types of films appear to be single phase some differences were observed in the compositional analysis as shown in figure 5. Figure 5a shows MiniSIMS depth profiles of a selenised film that shows the CIAS phase. The profiles of the elements Cu, Al and Se are seen to be uniform with depth but the In trace is slightly decreasing from half way through the film.

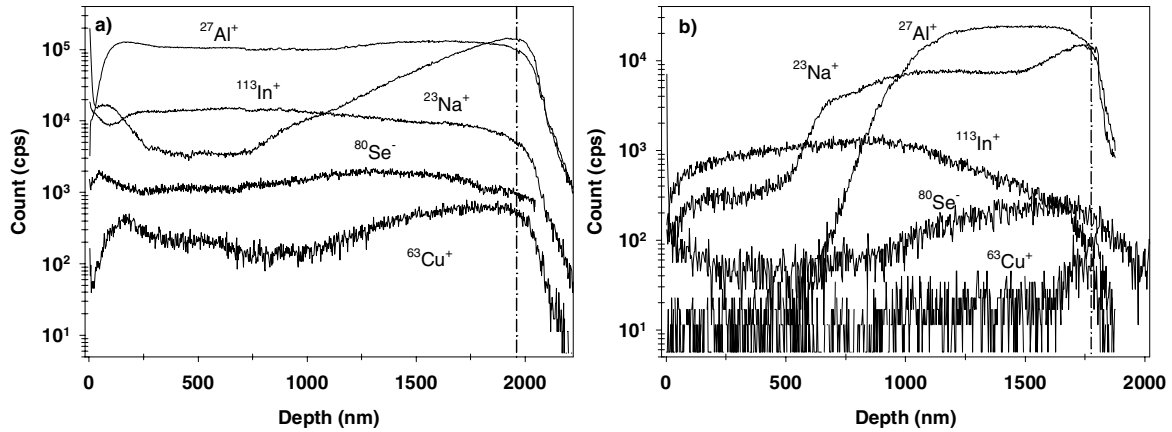


Figure 5. MiniSIMS depth profiles of selenised precursor films ($x = 0.18$). a) For a film showing the CIAS quaternary phase and b) for a film behaving like CIS. The vertical lines mark the start of the interface with the glass substrate.

The decrease in the $^{113}\text{In}^+$ signal is significantly more pronounced for the film yielding a pure CIS XRD pattern (figure 5b). The other major difference is the lower Al concentration at the front of the film and a higher concentration profile towards the back of the film. The film of figure 5b shows an Al profile concentration similar to a step function while other films exhibited a more gradual increase. If this material is considered to be a bilayer structure then the SIMS RSFs for the elements may differ from one layer to another. This offers an explanation of the slight variation in Cu and Se traces but also the In trace. To some extent this could also be true for figure 5a. The apparent film structure (figure 5b) actually consists of two CIAS layers with x increasing towards the substrate. For this type of films reflectance measurements confirmed the low bandgap material at the top being either CIS or CIAS but with a low x . The Na profile of figure 5a conforms to what is usually observed for CIS-based material grown on glass whereas the Na profile of figure 5b is dramatically different and resembles that seen when films are grown on Mo. In this case the Al rich layer behaves like Mo and controls the rate of diffusion of Na into the layers from the glass.

We therefore suggest that the CIAS films consist of a mixture of at least two CIAS phases with slightly different compositions. This is supported by the fact that an asymmetry on the lower 2θ side is observed on the XRD pattern (figure 3b). This implies the presence of a secondary CIAS phase. However, evidence of a CIAS mixture with two different compositions is further supported by XRD patterns of some films with high Al content. In these an extra peak can be seen on the high 2θ side of the CIAS (112), (220/204) and (116/312) reflections.

Peaks at even higher reflection angle appeared to be very broad compared to the usual CIS/CIAS material. XRD fitting revealed that indeed those spectra could be matched with the use of 2 peaks for each reflection. Optical measurements also revealed two absorption edges.

The films produced were tested electrochemically for their photoresponse and suitability for solar devices. The CIAS responded well even with no surface etching. The measured output current is improved when the surface of the film is subject to the cyanide etch and the best response is observed after a 60 sec etch time for which the current is doubled. For longer etch time the output current slowly decreases.

CONCLUSIONS

The Cu/In/Al metallic precursors were produced by magnetron sputtering had good lateral uniformity and good depth uniformity of the constituent elements throughout the film thickness. Metallic precursors have been selenised produce single phase, chalcopyrite structure CIAS layers with good crystallinity. The layers were also conformal and highly adhesive to the Mo-coated glass substrates. The electrochemical studies also clearly indicated that the photoresponses from the best CIAS layers produced were high and these layers hence have excellent potential for producing efficient solar cell devices. Further work is required to improve the reproducibility of forming single phase CIAS using the 2-stage method, especially to avoid the formation of multiple phase CIAS that can form under some conditions of synthesis.

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